Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes

Regine Röthlisberger[1,2], Manuel A. Hutterli[3], Eric W. Wolff[2], Robert Mulvaney[2], Hubertus Fischer[4], Matthias Bigler[1], Kumiko Goto-Azuma[5], Margareta E. Hansson[6], Urs Ruth[4,7], Marie-Louise Siggaard-Andersen[8], Jørgen P. Steffensen[8]

[1]Climate and Environmental Physics, University of Bern, Switzerland
[2]British Antarctic Survey, Natural Environment Research Council, Cambridge, United Kingdom
[3]Dept. of Hydrology and Water Resources, University of Arizona, Tucson AZ, USA
[4]Alfred Wegener Institute of Polar and Marine Research, Bremerhaven, Germany
[5]National Institute of Polar Research, Tokyo, Japan
[6]Dept. of Physical Geography and Quaternary Geology, Stockholm University, Sweden
[7]Institut für Umweltphysik, Universität Heidelberg, Germany
[8]Dept. of Geophysics, University of Copenhagen, Denmark

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Abstract

A compilation of nitrate (NO_3^-) data from Greenland has shown that recent NO_3^- concentrations show a temperature-dependence similar to the one seen in Antarctica. Except for sites with very low accumulation rates, lower temperatures tend to lead to higher NO_3^- concentrations preserved in the ice. Accumulation rate, which is closely linked to temperature, might influence the concentrations preserved in snow as well, but its effect cannot be separated from the temperature imprint. Processes involved in NO_3^- deposition are discussed and shown to be temperature- and/or accumulation rate-dependent. Apart from scavenging of nitric acid (HNO_3) during formation of precipitation, uptake of HNO_3 onto the ice crystal's surface during and after precipitation seems to contribute further to the NO_3^- concentrations found in surface snow. Post-depositional loss of NO_3^- from the top snow layers is caused by release of HNO_3 and by photolysis of NO_3^-. It is suggested that photolysis accounts for considerable losses at sites with very low accumulation rates. Depending on the site characteristic, and given that the temperature- and accumulation rate-dependence is quantified, it should be possible to infer changes in atmospheric HNO_3 concentrations.

Introduction

The nitrate (NO_3^-) record in polar ice cores is expected to contain information about past atmospheric concentrations of nitrogen oxides (NO_x = NO + NO_2) due to the close link of NO_3^- and NO_x. The increase in atmospheric NO_x concentrations in the northern hemisphere caused by rising fossil fuel combustion since approximately 1940, for example, is reflected in higher NO_3^- concentrations in Greenland snow [*Neftel and others*, 1985]. However, past studies have shown that factors other than atmospheric NO_x concentrations influence NO_3^- records as well [*Wolff*, 1995]. In Greenland as well as in Antarctica, reversible deposition of NO_3^- and net losses in the top snow layers have been observed. It has been suggested that either re-evaporation of nitric acid (HNO_3) [*Mulvaney and others*, 1998; *Dibb and others*, 1998; *Röthlisberger and others*, 2000] or photolysis of NO_3^- in the top few centimeters of the snowpack [*Honrath and others*, 2000; *Jones and others*, 2000] cause such post-depositional alterations.

In earlier studies, relationships between NO_3^- and accumulation rate have been proposed [*Herron*, 1982; *Legrand and Kirchner*, 1990; *Yang and others*, 1995], with generally higher accumulation rates associated with lower NO_3^- concentrations and higher NO_3^- depositional fluxes. In a more recent study based on a macroscopic deposition model, *Fischer and others* [1998] found a second-order polynomial dependence of average firn concentration and inverse snow accumulation.

Based on a compilation of NO_3^- data from more than 50 Antarctic sites covering various temperature and accumulation regimes, it has recently been suggested that temperature is also a key parameter in defining NO_3^- concentrations in Antarctic snow and ice, with lower temperatures leading to higher NO_3^- concentrations preserved in the snow [*Röthlisberger and others*, 2000]. Elevation has also been linked to NO_3^- concentrations, both for Greenland and Antarctica [*Yang and others*, 1996; *Mulvaney and Wolff*, 1994], but no statistically significant relationship has been found in a more recent study [*Kreutz and Mayewski*, 1999]. The inherent connection between temperature, accumulation rate and elevation makes it difficult to distinguish between the separate effects and thus no firm conclusions about their relative importance have so far been reached.

Here, we give a detailed description of the processes involved in NO_3^- re-emission and a discussion of how temperature and accumulation rate affect those processes. In analogy to the compilation of NO_3^- data from Antarctic sites, NO_3^- data from many Greenland sites have been gathered in order to illustrate the effect of temperature. Also, we outline how calcium (Ca^{2+}) can inhibit NO_3^- re-emission.

Another aspect that has been discussed lately dealt with the effect of snow layers containing large amounts of sulfuric acid (H_2SO_4) of volcanic origin on NO_3^- concentrations. Most studies focused on a few well known volcanic eruptions during the Holocene which showed post-depositional displacement of NO_3^- away from the H_2SO_4 peak. This behaviour has been found in single events in Greenland and Antarctica [*Clausen and others*, 1997; *Legrand and Kirchner*, 1990; *Röthlisberger and others*, 2000]. However, the mechanisms leading to this effect are only vaguely understood and hypotheses have not been tested on a large number of cases, because of a lack of sufficient high-resolution data.

In this paper, new high-resolution data from the NGRIP (North Greenland Ice Core Project) ice core are used to investigate the effect of volcanic H_2SO_4 on NO_3^- in more detail. Volcanic events from the early Holocene, the Last Glacial Maximum (LGM) and some earlier glacial periods are compared and a hypothesis of the mechanism is given.

Data

Many of the NO_3^- data used in this paper are compiled from earlier studies (see Table 1 for references). Furthermore, data from selected sections of the NGRIP ice core (75.1°N, 42.05°W, 2978 m above sea level) are presented. These sections were analyzed during the NGRIP 2000 field season with a continuous flow analysis (CFA) system, as described in *Röthlisberger and others* [2000]. Among other compounds, nitrate (NO_3^-), sulphate (SO_4^{2-}), and calcium (Ca^{2+}) have been measured at a resolution of approximately 1 cm.

NO_3^- – temperature – accumulation rate

In Fig. 1 average NO_3^- concentrations for different Greenland locations are indicated. In order to account for the anthropogenic increase in NO_3^- concentrations in Greenland, the data have been split into two separate sets, one indicating concentrations from before 1940, which are unaffected by the anthropogenic emissions, and one from after 1970. The data and the appropriate references are listed in Table 1. For both pre-1940 and post-1970, a decreasing trend in NO_3^- concentration with increasing temperature is found (Fig. 2).A similar trend has been found in Antarctica [*Röthlisberger and others*, 2000], where also generally higher concentrations are found at sites with lower temperatures, except for very low accumulation sites such as for example Dome C. At Dome C, the concentrations in the top few centimeters can be very high (up to 1000 ppb), but at greater depths, only 15 ppb are preserved, despite the low temperatures (annual mean temperature $\approx -54°$ C).

If NO_3^- concentrations are plotted against accumulation rate, higher NO_3^- concentrations are found at sites with lower accumulation rates (Fig. 3), but again, NO_3^- concentrations at very low accumulation sites do not agree with the general trend. Considering the close relationship between temperature and accumulation rate (Fig. 4),it seems difficult to separate the effect of temperature and accumulation rate on NO_3^- concentrations. Only a detailed consideration of the underlying microphysical processes allows for assigning a temperature or accumulation rate dependence.

In the following discussion, we analyse the temperature and accumulation rate dependence of processes involved in NO_3^- deposition and re-emission, aiming for a better understanding of:

- the cause of the relationship between NO_3^- concentrations and mean annual temperature and accumulation rate at a site

- the generally higher NO_3^- levels in summer snow than in winter snow
- the net loss of NO_3^- from snow after deposition

NO_3^- can either be predominantly incorporated in the bulk or adsorbed to the surface of a snow crystal, depending on the deposition pathway. In a cloud with a liquid water content of more than 0.01 $g\,m^{-3}$ and $pH > 1$, HNO_3 would be completely dissolved in water droplets due to its high solubility, leaving virtually no HNO_3 in the gas-phase [*Seinfeld and Pandis*, 1998]. Thus, in the case of liquid or mixed clouds, essentially all HNO_3 is removed from the gas-phase independent of the cloud temperature. While there is no specific information about the conditions at cloud level, typical liquid water contents of 0.1 $g\,m^{-3}$ and initial HNO_3 concentrations of 20 pptv in the air would lead to NO_3^- concentrations of approximately 350 ppbw in fresh snow. On the other hand, the co-condensation of HNO_3 and water (H_2O) molecules on ice crystals [*Thibert and Dominé*, 1998] would lead to a bulk concentration of 20 ppbw only. In the absence of liquid water, i.e. in ice clouds, the high NO_3^- concentrations found in surface snow could not be explained. However, *Abbatt* [1997] observed a temperature-dependence of adsorption of HNO_3 on ice surfaces with higher uptake at lower temperatures. For typical summer temperatures at South Pole (246 K, data obtained from http://www.cmdl.noaa.gov), the uptake capacity on fresh snow crystals exceeds the amount of HNO_3 available in the cloud, implying that at very cold temperatures where ice clouds predominate, essentially all HNO_3 in a cloud is bound to the surface of the snow crystal. While co-condensation, riming, and adsorption of HNO_3 determine the distribution of NO_3^- within the ice crystal, its concentration is defined by the initial atmospheric concentration of HNO_3 and the amount of condensed water in the cloud. An imprint of temperature is expected for surface uptake and co-condensation, but not for the HNO_3 taken up in liquid cloud droplets. Based on the results of *Abbatt* [1997], the snow crystals are expected to efficiently scavenge atmospheric HNO_3 on their way to the surface, potentially further increasing the NO_3^- concentration of the fresh snow.

Once on the ground, the formation of surface hoar frost (co-condensation), rime (deposition of supercooled fog droplets) as well as dry deposition (adsorption of HNO_3 onto the crystal's surface) leads to additional NO_3^- deposition to surface snow. For a given atmospheric HNO_3 concentration, the hoar frost NO_3^- concentration is determined by the water vapour concentration [*Thibert and Dominé*, 1998], which is mainly a function of temperature T. Assuming that the relative humidity at the site is similar throughout the year, the NO_3^- concentration should depend linearly on 1/T in a first order approach. However, if assuming that the HNO_3 concentrations in the atmosphere as in Table 2 are representative for the site, the estimated concentrations resulting from co-condensation are lower than observed surface snow concentrations, thus leading to dilution of the surface snow (Table 2). Rime deposition on the other hand, which is likely to remove all HNO_3 from the air, shows similar concentrations to fresh snow, provided that the atmospheric HNO_3 concentration is similar to the one at cloud level. A net dry deposition of HNO_3 (adsorption of HNO_3 onto snow crystals) has the potential to increase the NO_3^- concentration in snow. However, it will only contribute where the surface is undersaturated, i.e. at very cold sites and

during winter. The contribution in winter is small, due to low atmospheric HNO_3 concentrations. During the summer, the contribution of dry deposition to the NO_3^- concentrations in snow at South Pole might be considerable. However, according to *Hauglustaine and others* [1994], the dry deposition velocity of 0.5 $cm\,s^{-1}$ for HNO_3 on snow has to be considered as an upper limit. At sites with higher accumulation rates, a specific surface snow layer is buried more rapidly, leaving less time to adsorb additional HNO_3 from the atmosphere, given that no saturation has been reached. Therefore, a tendency for higher concentrations at lower accumulation rates is expected.

Besides the diluting effect of co-deposition, processes capable of reducing the NO_3^- concentration in snow are desorption of HNO_3 from the snow crystal [*Mulvaney and others*, 1998; *Dibb and others*, 1998; *Röthlisberger and others*, 2000] and photolysis [*Honrath and others*, 2000; *Jones and others*, 2000]. In both cases, the NO_3^- ion has to be at the surface of a snow crystal, since photolysis of NO_3^- in the bulk is not effective [*Dubowski and others*, 2001]. If a NO_3^- ion recombines with a H^+ ion to form HNO_3, it then may desorb into the firn air and eventually diffuse into the air above the snow. Diffusion of NO_3^- in ice has been investigated by *Thibert and Dominé* [1998], who found that diffusion of NO_3^- in ice is slower at colder temperatures with the diffusion coefficient D given by $D = 1.37 \times 10^{-2610/T} cm^2 s^{-1}$ with T being the temperature in K. During the summer, the typical time a NO_3^- molecule needs to reach the ice surface (diffusion length of 40μm, corresponding to an average crystal radius [*Harder and others*, 1996]) is of the order of a couple of hours (e.g. Neumayer) to a few days (e.g. South Pole).

The solubility of NO_3^- in ice has been determined for various temperatures [*Thibert and Dominé*, 1998]. For summer conditions, not only the surface snow but also deeper layers are supersaturated with respect to the solubility of NO_3^- in ice (Table 2). In the case of South Pole, the surface remains undersaturated, suggesting that NO_3^- that is expelled from the bulk is simply transferred to the surface without affecting the NO_3^- concentration. At warmer sites (e.g. Neumayer or Summit), the ice surface also might become supersaturated during the summer, leading to release of HNO_3 from the snow into the interstitial air. From a thermodynamic point of view, warmer temperatures during the summer should facilitate the release of HNO_3 from the ice surface. But according to the uptake experiment of *Abbatt* [1997], only up to 25% of the HNO_3 that has been taken up are released again afterwards. However, the emphasis of his study was laid on the uptake rather than the release of HNO_3 and a temperature-dependence of the release has not been discussed. Once released from the snow crystal's surface, the HNO_3 molecule might make its way out of the snowpack, leading to a net loss of NO_3^- in the snow. The molecular diffusion of HNO_3 in the interstitial air is temperature dependent as well, but probably this is not the limiting factor controlling the transfer out of the snowpack. It is conceivable that temperature-dependent, repeated adsorption and subsequent desorption of a HNO_3 molecule on ice crystals will determine the removal from the snowpack.

Photolysis of NO_3^- in the top snow layers results in the production of nitrogen dioxide (NO_2) and hydroxyl radical (OH). NO_2 is not expected to interact with the

surrounding snow but to be mixed into the boundary layer rather quickly, leading to a NO_3^- depletion in surface snow. The influence is presumably largest at low accumulation sites, where surface snow is exposed to sunlight for a long time. Furthermore, photolysis should become more efficient at lower latitudes due to more incoming UV radiation. At Dome C, the top few centimeters of snow seem to reach saturated surface coverage (concentrations in the range of several 100 ppbw) [*Röthlisberger and others*, 2000]. Deeper layer are then dramatically undersaturated considering surface coverage and solubility in the bulk. No quantitative estimate of how much NO_3^- can be lost by photolysis has been made so far. It therefore remains unclear whether photolysis alone can account for the NO_3^- profile seen in the snow at Dome C. The estimate of the maximum surface uptake relies very much on the surface area in snow and might change due to recrystallization, which has not yet been taken into account.

Although elevation may affect the atmospheric HNO_3 concentration, there is no obvious mechanism by which it can have a direct physical influence on post-depositional processes. A minor influence is expected on the photolysis rate due to changes in the irradiance with altitude and on the gas-phase diffusion due to lower pressure, but both effects might only slightly modulate the changes in NO_3^- concentrations.

Interactions of NO_3^- with dust

Recent studies have reported that NO_3^- and Ca^{2+} concentrations are correlated in ice from the last glacial period from Vostok and Dome C [*Legrand and others*, 1999; *Röthlisberger and others*, 2000]. During the last glacial period, the Ca^{2+} deposited on the east Antarctic plateau is mainly of terrestrial origin and can thus be used as a proxy for dust. It has been suggested that the reaction of HNO_3 and $CaCO_3$ to form $Ca(NO_3)_2$ prevents NO_3^- from being released from the snow into the gas-phase.

In principle, the reaction could take place in the atmosphere or in the snow. For it to happen in the atmosphere, high dust concentrations would need to be in the same season as the maximum nitrate concentrations. A recent paper that studied the reaction of $CaCO_3$ with HNO_3 derived a formula for the lifetime for removal of HNO_3 by dust [*Hanisch and Crowley*, 2001]. Based on this, and using very rough estimates for the surface area of dust (assuming spherical particles of 1 μm diameter, a typical density of 2 $g\,cm^{-3}$, and atmospheric dust concentrations of 10 $ng\,m^{-3}$), we can estimate an HNO_3 lifetime versus removal by dust in the present day Antarctic atmosphere of around 50 days. This is unlikely to be important relative to other removal processes. However, this could be reduced to 2 days under the dustier conditions of the LGM, and in Greenland under LGM conditions one could estimate a lifetime for this removal of only a few hours. It seems possible therefore that under LGM conditions, much of the atmospheric HNO_3 could be converted to aerosol calcium nitrate in the atmosphere. In addition, the reaction to form $Ca(NO_3)_2$ might take place in the snow, in which case HNO_3 has to make its way to the snow layer where the Ca^{2+} has been deposited and, if Ca^{2+} is inside the snow grain rather than on its surface, diffuse through it.

Influence of volcanic H_2SO_4 on NO_3^-

As shown lately in an Antarctic high-resolution record from Dome C [*Röthlisberger and others*, 2000], H_2SO_4 of volcanic origin can cause NO_3^- to move in the ice. Several examples of very low NO_3^- concentrations coinciding with H_2SO_4 peaks and increased NO_3^- concentrations above and below this layer have been found in the Dome C as well as the NGRIP record (Fig. 5a). At Dome C, the effect is first seen at 12 m depth, where the deposits of the Tambora eruption (1815 A.D.) are located. This indicates that the processes involved take place or at least start in the firn.

Our hypothesis of the mechanism for NO_3^- displacement in the firn relies on similar processes as described above, as it includes diffusion of HNO_3 in the firn air. The high concentration of H_2SO_4 in a volcanic layer causes the equilibrium of $H^+ + NO_3^- \rightleftharpoons HNO_3$ to shift towards the right hand side, as a large amount of H^+ from the H_2SO_4 is present. Therefore, a locally elevated concentration of HNO_3 in the firn air is caused, which prompts gas-phase diffusion of the HNO_3 away from the volcanic layer towards either side. In adjacent layer with no excessive H_2SO_4, HNO_3 favours dissociation into H^+ and NO_3^-, thus maintaining the gradient in the firn air by removing HNO_3 from the gas-phase. It is possible that the movement of NO_3^- progresses via a different mechanism in the ice after pore close-off, possibly by diffusion of ions in the veins.

Fig. 5b shows an event where no NO_3^- displacement occurred. In this section, large amounts of alkaline material are present in the ice, as seen by the high Ca^{2+} and negligible H^+ concentrations. In the context of the above hypothesis, the high concentrations of alkaline material (presumably $CaCO_3$) neutralize the H_2SO_4 and prevent the formation of HNO_3. The assumption that in this case H_2SO_4 undergoes some reactions is supported by the significantly narrower SO_4^{2-} peak compared to the ones seen in acid ice (P. Barnes, pers. communication).

Our hypothesis is challenged by the example shown in Fig. 5c. Although a lot of excess H_2SO_4 is present and far too little Ca^{2+} to compensate, no marked NO_3^- displacement is seen. It is possible that the Ca^{2+} was unable to neutralize the H_2SO_4, but that it managed to bind NO_3^- thus preventing it from being transferred into the gas-phase. The occurrence of ice layers limiting HNO_3 diffusion in the interstitial air is rather unlikely in NGRIP.

Conclusions

The spatial distribution of nitrate concentrations in Greenland is shown to be strongly related to site temperature, just as it is for Antarctica. Because temperature and snow accumulation rate are so closely linked, we cannot determine which of these factors is the one exerting physical control on the concentrations seen. In either case, the relationship changes at the very lowest accumulation rates, where it is clear that post-depositional losses are the dominant control on the sub-surface concentration.

By examining the individual processes that could contribute to the nitrate concentration in snow, we find that many of them are indeed temperature-dependent, with higher concentrations predicted at lower temperatures, as observed. Some processes

could also depend on the accumulation rate, if a longer exposure time at the surface allows additional uptake. Of the processes identified, either uptake by liquid droplets in cloud, if present, or uptake onto the ice surface in the cloud or after deposition can lead to concentrations in fresh snow that are as high or higher than those observed. However, the role of surface uptake at higher temperatures, as encountered in coastal Antarctica and in Greenland in summer, needs to be quantified. Co-condensation of nitric acid and water, and dissolution of nitric acid within the ice lattice appear to give concentrations that are too low compared to those observed. This suggests tentatively that surface uptake and retention might be rather important in determining the concentrations we see. This process has a temperature dependence (approximately threefold greater uptake at −55°C compared to −25°C [*Abbatt*, 1997]) similar to that seen in Fig. 2. However, according to *Abbatt* [1997], the uptake is not dependent on the nitric acid concentration in air. The higher nitrate concentrations in post-1970 Greenland snow compared to pre-1940 snow suggests that the snow concentration is somehow related to atmospheric concentrations, and we suggest that this is simply a question of limited supply to the ice surface, because nitric acid is scavenged so efficiently. In that case, a temperature- and accumulation rate-corrected Holocene nitrate ice core record of a site with adequate snow accumulation rate should reflect the flux of nitrate to the surface, which should in turn be related to atmospheric NO_x input.

For sites with very low accumulation rate, losses, possibly due to photolysis, control the concentration seen in the Holocene in such a dominant way that it is unlikely that information about atmospheric nitrate or NO_x can be extracted. Once the ice becomes less acidic (in the last glacial period), the concentration of nitrate seems to be strongly controlled by the calcium or dust content of the atmosphere, and the deposition processes might be significantly altered. The ratio of nitrate to dust might give clues to the past nitrate content of the atmosphere, although in this case it is probable that the nitrate uptake is determined by the content of the atmosphere over the whole transport route of dust from its source to the deposition site, and is not closely related to the local nitrate concentration at the ice core site.

A number of laboratory and field experiments would help to test the above hypotheses. Laboratory uptake experiments, similar to those carried out at 248 K and below [*Abbatt*, 1997], are needed at higher temperatures, appropriate to summer temperatures at coastal Antarctic or Greenland sites. Laboratory experiments would also allow an assessment of whether photolysis can account for the magnitude of nitrate losses at low accumulation sites. Field measurements of the nitric acid content of the atmosphere are lacking for most sites, and particularly for winter. Experiments that follow the evolution of concentration from fresh snow to depth in individual layers are also required.

In summary, the factors that control nitrate concentration in ice cores are complex, and interpretation is likely to involve different factors for different locations and time periods. However, if the factors controlling deposition and loss can be better understood, it may still be possible, in some cases, to reconstruct information about the important NO_x cycle in the past.

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Site and Ref.	Lat. °N	Long. °W	Altitude m	Temp. °C	Acc. $g\,cm^{-2}\,a^{-1}$	NO_3^- pre-1940 ppb	# years	NO_3^- post-1970 ppb	# years
1988-8[1]	64.6	43.7	2550	-19.9	57			94	2
1988-7[1]	64.8	44.1	2745	-22.0	38			90	3
Dye 3 18C[2], 20D[3]	65.0	44.9	2617	-22.3	41	53,55	174[a],30[c]	100,122, 132	15,5, 15
Dye 3 [2,4]	65.2	43.8	2491	-20.0	49	44,52, 52	10[b],11[b], 220[h]	86,114 137	6,7, 2
1988-4[1]	66.6	45.5	2130	-18.6	30			117	2
1988-5[1]	67.0	44.5	2250	-20.3	33			115	4
1988-6[1]	67.2	43.8	2450	-21.6	36			108	6
EGIG T05[5]	69.9	47.3	1910	-18.0	46			118	5
EGIG T09[5]	70.0	46.3	2170	-20.0	41			134	9
EGIG T13[5]	70.2	45.0	2380	-22.6	46			107	8
Milcent[2]	70.3	44.6	2410	-22.0	49	61	7[g]		
EGIG T17[5]	70.4	44.1	2530	-23.8	44			117	9
EGIG T21[5]	70.6	43.0	2700	-24.8	44			112	9
Site A[2,6]	70.6	35.8	3092	-29.4	29	45,64, 70	3[d],2[c], 19[b]		
Site D[6]	70.6	39.6	3018	-28.3	34	73	19[b]		
EGIG T27[5]	70.8	41.6	2870	-26.6	39			113	9
EGIG T31[5]	70.9	40.6	2970	-27.5	34			133	10
EGIG T41[5]	71.1	37.9	3150	-29.5	25			144	12
Crete[2]	71.1	37.3	3172	-30.0	28	60,80	60[e],2[g]		
EGIG T43[5]	71.1	37.3	3172	-30.1	23			144,146	8,14
EGIG T47[5]	71.2	36.0	3099	-29.9	22			143	8
Renland[7,8]	71.3	26.7	2340	-18.0	42	64,88	5[g],9[c]		2
EGIG T53[5]	71.4	32.5	2864	-28.0	23			134	9
1987-2[1]	71.6	38.1	3157	-30.4	25			128	5
EGIG NST08[5]	71.9	37.8	3220	-31.0	23			153	5
1987-3[1]	71.9	39.8	3145	-30.3	30			123	2
1987-5[1]	72.0	37.5	3187	-31.5	22			130	6
EGIG T61[5]	72.2	32.3	2812	-28.8	19			144	8
1987-1[1]	72.3	37.9	3170	-31.3	22			124	10
1987-4[1]	72.4	40.2	3146	-31.5	27			130	5
GISP2 ATM[1]	72.4	38.8	3200	-32.0	24			120,130, 135,138	3,5, 9,3
EGIG T66[5]	72.5	30.8	2678	-25.7	17			159	6
GISP2[1,9,10]	72.6	38.5	3200	-31.0	22	61,70	410[a],650[a]	108,125, 126,135, 136,149 149,167	30,7, 3,6, 6,2, 2,4
GRIP[5,11,12]	72.6	37.6	3232	-31.6	20	68	30[c]	130,138, 142	5,9, 21
1987-7[1]	72.6	35.9	3190	-33.1	18			157	8
1990-2[1]	72.8	36.5	3200	-33.8	17			136	1
1987-6[1]	73.0	37.7	3224	-33.8	17			148	8
NGT01[13]	73.0	37.7	3223	-34.3	16			143	13
NGT03 B16[13]	73.9	37.6	3040	-34.6	12	85	40[a]	132	23
North Central[2]	74.6	39.6	2930	-32.0	13	83,112	9[f],21[b]	164	5
NGT05[13]	74.9	37.6	2873	-35.3	11			189	12
NGRIP[8,14]	75.1	42.1	2978	-30.9	17	81	156[a]	149,161	5,11
NGT12[13]	75.7	36.4	2671	-34.2	10			161	14
NGT14 B18[13]	76.6	36.4	2508	-35.0	10	73	40[a]	128	23
C. Century[2]	77.2	61.1	1880	-24.4	35	46,65, 71	10[g],13[d], 100[h]	120	2
1988-1[1]	77.2	60.7	1650	-24.6	29			101	7
1988-2,3[1]	77.2	59.2	1700	-23.7	31			96,107	4,2
C. Century II[2]	77.2	60.8	1910	-24.7	35	52	13[b]		
NGT37 B26[15]	77.3	49.2	2598	-30.0	18	69	440[a]	110	24
NGT18[13]	77.5	36.4	2319	-32.6	11			158	14
NGT23 B20[16]	78.8	36.5	2147	-31.5	10	83	1130[a]	155	24
NGT27 B21[13]	80.0	41.1	2185	-29.6	11	80	40[a]	126	24
Hans Tausen[8]	80.5	37.5	1271	-21.0	10	74	30[c]	91	3

Table 1: Temperature, accumulation rate and NO_3^- concentration for Greenland locations used in this study.

[1]Yang and others (1996), data obtained from http://nsidc.org, [2]Clausen and Langway (1989), [3]Mayewski and others (1990), [4]Neftel and others (1985), [5]Fischer and Wagenbach (1996), [6]Steffensen (1988), [7]Hansson (1994), [8]H.B. Clausen, personal communication (2001), [9]Yang and others (1995), [10]University of Arizona, unpublished data, [11]Clausen and others (1997), [12]Steffensen and others (1996), [13]Fischer and others (1998), [14]L.B. Larsen, personal communication (2001), [15]Hausbrand (1998), [16]Bigler (2000).

[a]Continuous record up to 19940, [b]20th century, before 1940, [c]19th century, [d]18th century, [e]11 to 18th century, [f]15th century, [g]13th century, [h]Holocene

	Summit		Neumayer		South Pole	
	Summer	Winter	Summer	Winter	Summer	Winter
Pressure (Pa)	67000		99000		68000	
Acc. rate ($g\,cm^{-2}\,a^{-1}$)	20		34		8.5	
Temperature (K)	259	230	269	247	246	208
Relative Humidity	0.75	0.75	0.8	0.8	0.75	0.6
HNO_3 atm. (pptv)	20	1	6	1	20	1
NO_3^- snow (ppbw)	120		50		100	
Co-Condensation (ppbw)	7	9	1	2	26	160
Solubility in ice (ppbw)	19	29	8	12	40	150
Surface uptake (ppbw)		1900		780	840	3300
Dry deposition (ppbw)	30	2	8	1	77	5

Table 2: Estimates of NO_3^- concentrations in snow due to different deposition mechanisms. The meteorological data are from automatic weather stations, the atmospheric HNO_3 summer concentrations are from *Dibb and others* [1994] and *Jones and others* [1999]. For South Pole, atmospheric concentrations of the same order of magnitude as in Summit have been assumed. The HNO_3 winter concentration has only been measured at Neumayer and has been found to be approximately 1 pptv (R. Weller, personal communication). In the absence of measurements for the other sites, we assume the winter concentrations at Summit and South Pole to be the same as in Neumayer. The calculations for co-condensation and solubility in ice are based on *Thibert and Dominé* [1998]. Surface uptake was estimated using a linear regression through the values for temperature-dependent uptake found by *Abbatt* [1997] and assuming a typical surface area of 4000 $m^2\,m^{-3}$ [*Narita*, 1971]. Temperatures higher than 248 K have not been included in the study of surface uptake, therefore the estimates for surface uptake in Summit and Neumayer during summer are missing. Dry deposition was calculated assuming a dry deposition velocity of 0.5 $cm\,s^{-1}$ [*Hauglustaine and others*, 1994].

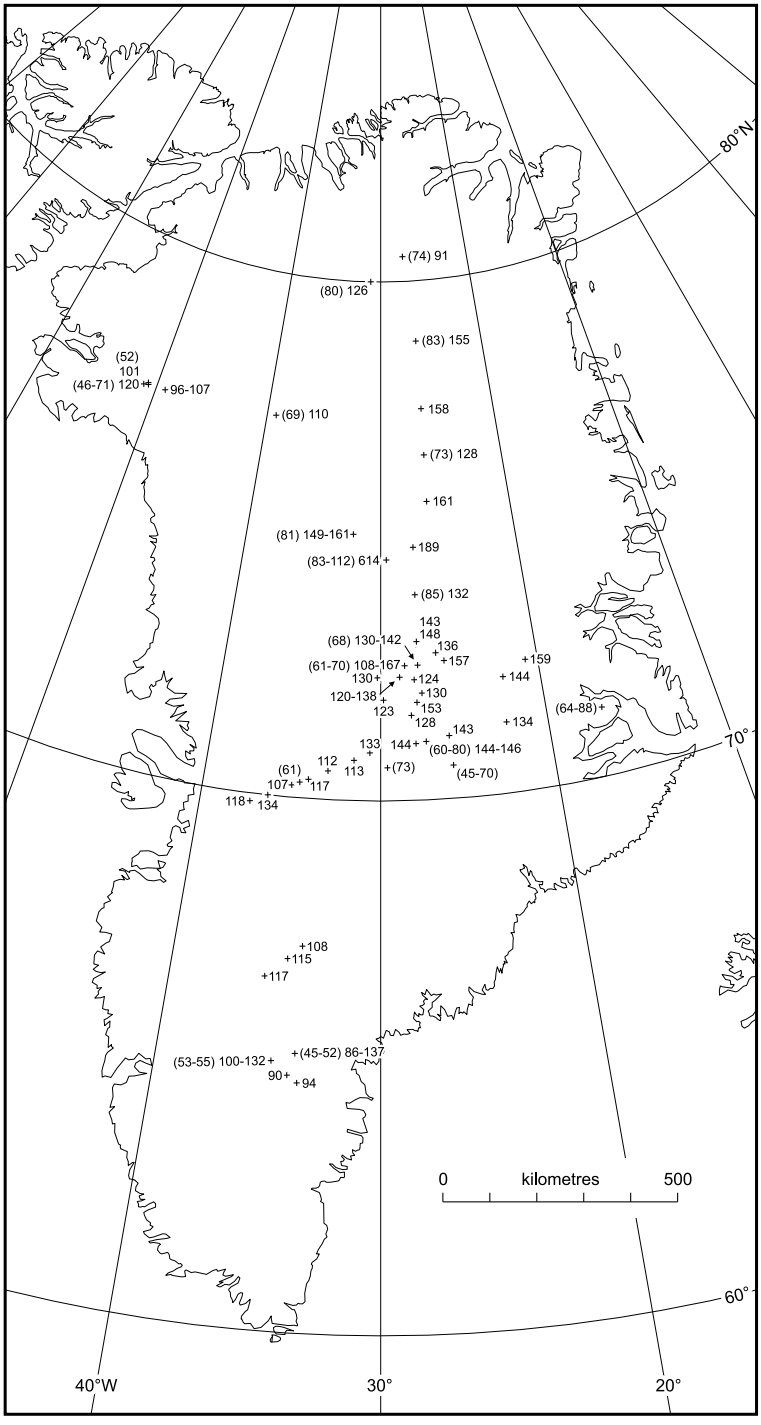

Figure 1: Spatial distribution of NO_3^- across Greenland. Concentrations in snow deposited before 1940 are shown in parentheses, the other values correspond to concentrations in snow deposited after 1970. All concentrations are in ppb.

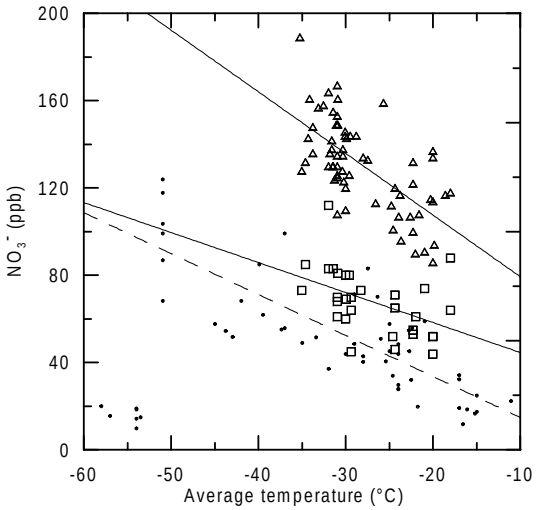

Figure 2: NO_3^- concentrations versus average temperatures in Greenland and Antarctica with linear trends (triangles (post-1970), squares (pre-1940) and the solid lines: Greenland; dots and dashed line: Antarctica). The data points at temperatures below -52°C correspond to sites with very low accumulation rates and are not used for the calculation of the linear fit shown.

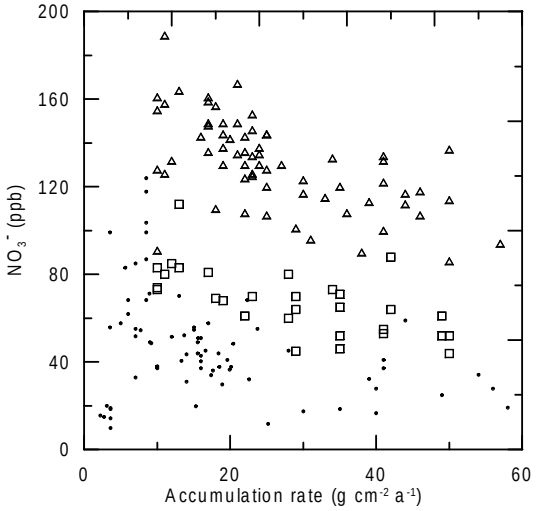

Figure 3: NO_3^- concentrations versus accumulation rate in Greenland and Antarctica (triangles: post-1970, squares: pre-1940, dots: Antarctica).

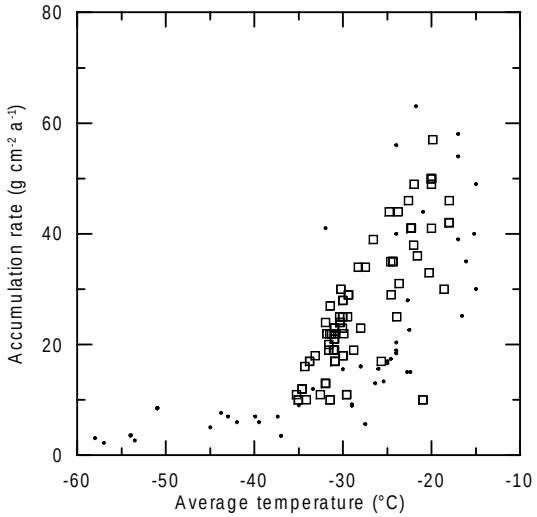

Figure 4: Accumulation rate versus average temperatures in Greenland and Antarctica (squares: Greenland, dots: Antarctica).

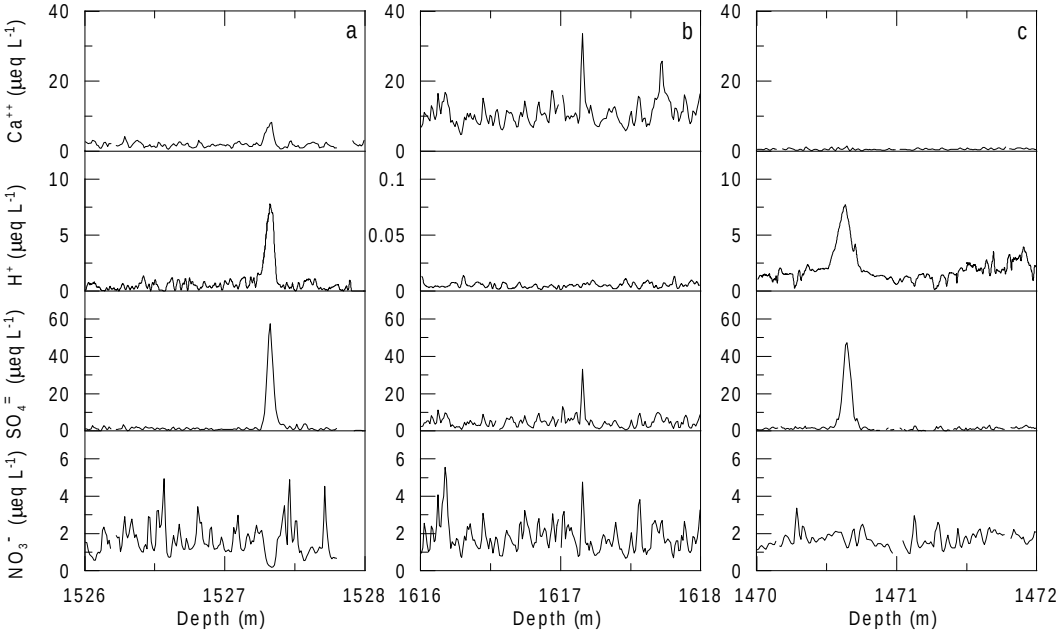

Figure 5: Examples of the influence of volcanic H_2SO_4 on NO_3^- in the NGRIP ice core. H^+ concentrations have been inferred from electrical conductivity measurements on the solid ice. Due to very low H^+ concentrations, the scale of the y-axis had to be adjusted for the section shown in (b). Of 28 events selected with SO_4^{2-} concentrations exceeding 20 μeq L^{-1}, 14 showed a pattern similar to (a), 12 similar to (b), and 2 similar to (c). The data is shown against depth, as the absolute age is not critical to the illustration of the effect and an absolute timescale is not yet available.